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Differential thermal analysis of some complexes of montmorillonite

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The heats of reaction for desorption of interlayer water, from montmorillonites in different cationic forms and equilibrated at different relative humidities, have been determined. The results favour a close correlation of desorption process between the divalent and the monovalent cationic forms within the observed range of relative humidities. The areas of the dehydroxylation loops have been measured, which supports the existing idea that the exchange cations have no influence on this process. It seems probable that the exothermic peak-temperature is dependent on the size of the exchange cations having the same charge.

1. Introduction

Montmorillonite is a three-layer lattice type of clay mineral having a high cation-exchange capacity due to its unbalanced charge distribution in the silicate layers. When heated to continuously elevated temperatures, a variety of reactions takes place in the montmorillonite lattices. At the initial stage, it loses the absorbed interlayer water within a range of temperatures, 100°C — 300°C. This water, influenced greatly by the exchange cations present, requires, however, a definite amount of energy for its complete elimination. Next, it is deprived of its structural water, i.e., (OH)- latticewater in the temperature range, 500°C, and finally the breakdown of the original structure takes place near the region of 900°C with the appearance of a new phase at higher temperatures. All these thermal reations are generally registered by the differential thermal analysis technique. The first endothermic peak system corresponding to the loss of inter-layer water form different cationic froms of the montmorillonite samples shows a fine structure which was investigated by Hendricks *et al* (1940). Mackenzie (1950) correlated the peak temperature of the high temperature component of this endothermic peak system and the hydration energy of the cations in montmorillonite. Mackenzie (1957) also gave a summary of the discussion on the loss of inter-layer water from various cationic froms of montmorillonite, by different authors. Also, it was reported by R. A. Rowland (1955) that the exothermic loop accompanied by the formation of new phases is largely controlled by the isomorphic substitution within the lattice and the nature of the exchange cation present in it.

In the present paper, the results obtained from the differential thermal analyses (d. t. a.) for the different complexes equilibrated at some specific relative humidities, are given in the tables. Again, the heats of reaction for the loss of interlayer water, which are proportional to the areas under the peaks (Kerr & Kulp 1948), have been determined. For this purpose, a heat of reaction scale was established for the differential thermal analyser. Also the areas of the second endothermic loops (dehydroxylation loops) for the different samples have been measured and they seem to be nearly constant. It is also noted, that when the chemical composition, *i.e.*, the isomorphic substitution of the mineral, remains the same, the peak temperatures of the exothermic reactions, for the different complexes of a particular sample, are dependent on the size of the exchange cation present.

2. Description of the samples and experimental procedure

It may be expected that the behaviour of montmorillonite is dependent upon its origin. The samples were, therefore, obtained from different deposits, which were bentonites originating from (i) England, (ii) Hanover, (iii) Assam, (iv) Kashmir (pink variety) and (v) Rajasthan. The different complexes of the minerals saturated with H^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+}ions were obtained by the same method as used by the author (1965). The samples in the above mentioned cationic forms derived from a particular bentonite were equilibrated under the same relative humidity as indicated by a Hair-hygrometer and at the same temperature for a period of three to four weeks.

The cation exchange capacity of the different bentonites were determined by the half saturated KCl-KOH method (Ganguli 1951).

The differential thermal analyses were performed with an unit consisting of a bell-type furnace which could be envelopingly placed on the refactory stand fitted with blocks of pure nickel having two holes, in which the samples were packed. The unit is also provided with a set of chromel-alumel thermocouples for the connection of the pyrometer indicator and the galvanometer. The pyrometer indicator shows the temperature of the furnace which can be regulated by adjusting the energy regulation device from outside.

The sensitivity of the apparatus in the lower region of temperatures was measured by using 7 mgm. of NH_4NO_3 with α-Al_2O_3 in one of the sample holes and 40 mgm. of AgI with 75 mgm. of Ca-bentonite in the other hole (Barshad 1952). The corresponding thermal breaks registered by the apparatus are shown in figure 1 with the necessary calculation for the sensitivity.

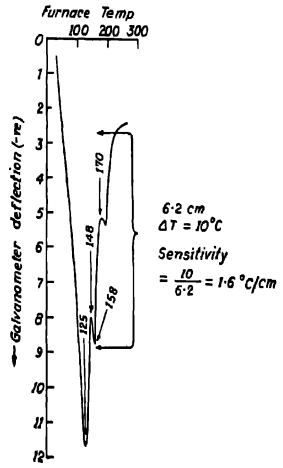

Figure 1. Sensitivity of the differential thermal analyser.

Also, the differential themal analyser was calibrated to establish a heat of reaction scale following the method of Barshad (1952). The substances used for this purpose were $CaSO_4.2H_2O$, $SrCl_2.6H_2O$ and $Na_2S_2O_3.5H_2O$ (hypo). In order to obtain the *d. t. a.* results of these hydrated salts and as well as the bentonite complexes, 250 mgms. of each sample were dispersed in calcined alumina (α-Al_2O_3) around the thermocouple in a volume of 0.465 cc. and was heated to continuously elevated temperatures. The rate of heating was 10°C/ minute and was maintained approximately constant throughout the range. The temperature of the furnace was recorded by the pyrometer indicator, and the temperature difference between the sample and the inert material (α-Al_2O_3) was recorded by a sensitive galvanometer connected in series with the differential thermocouple. The thermal reactions of the samples were then noted for different furnace temperatures and the results obtained for the various complexes of bentonites are given in tables 3-7.

The areas of the first and second endothermic peaks, as described by the contour of the peak and a line joining the two points of inflexion at the beginning and end of each peak, was measured by a planimeter (Rowland *et al* 1952) for different samples. The heats of reaction, for desorption of interlayer water from different samples of bentonites, were then calculated.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The cation exchange capacities of the different bentonites expressed in me/100 gm. are tabulated below.

TABLE 1

Sample	England	Hanover	Assam	Kashmir (pink variety)	Rajasthan
Cation exchange capacity.	100	86	90	100	80

The heat of reaction data for the calibration of the differential thermal analyserare given in table below.

TABLE 2

Sample	Calculated value of heat of reaction (cal/gm).	Peak area for 250 mgm of sample (sq. mm.)	Heat of desorption per 250 mgm. of sample per sq. mm.	Average heat of desorption per gm. of sample per sq. mm.
$CaSO_4.2H_2O$	164	128	0.32 cal	
$BaCl_2.2H_2O$	127	96	0.34 cal	
$Na_2S_2O_3.5H_2O$ (hypo)	296	220	0.33 cal	1.28 cal
$SrCl_2.6H_2O$	343	283	0.31 cal	

The values of the cation exchange capacities for the different samples of bentonite, shown in table 1, agree with the generally accepted values (Grim 1953) for the montmorillonite group.

The d. t. a. curves drawn for the different complexes and the nature of the thermal reactions agree with the standard curves for montmorillonite (Kerr *et al* 1949). They also show a loss by the mineral, of the adsorbed interlayer water within the range of temperatures, 100°C—300°C. Beyond this it has been found that the mineral loses the structural water in the temperature range—500°C—800°C. Also, the exothermic peaks for the different complexes appear within a range of temperatures 900°C—1000°C depending on the nature of the exchange cations present.

The differential thermal analyses data for different samples of bentonite are given in the following tables 3-7 showing the values of the

TABLE 3. RELATIVE HUMIDITY=20%, TEMPERATURE=30°C.

Complexes of bentonite from England.	Desorption temperature in d.t.a. (centigrade)	Heat of desorption (△H) (cal/gm.)	Dehydroxylation temperature in d. t. a (centigrade)	Peak area of dehydroxy-lation. (sq. mm.)	Peak temperature of exothermic reaction (centigrade)
H-bentonite	70-210	96.00	650-750	24	940
Li- ,,	60-215	51.20	600-720	25	945
Na- ,,	70-170	35.64	620-760	24	970
K- ,,	70-150	19.20	650-770	25	975
Mg- ,,	70-300	93.44	650-750	22	960
Ca- ,,	60-210	76.80	650-760	22	970
Ba- ,,	70-200	44.80	600-750	22	980

TABLE 4. RELATIVE HUMIDITY=25%, TEMPERATURE=31°C.

Complexes of bentonite from Kashmir (pink variety)	Desorption temperature in d.t.a (centigrade)	Heat of desorption (△H) (cal/gm.)	Dehydroxylation temperature in d. t. a. (centigrade)	Peak area of dehydroxyla-tion (sq. mn.)	Peak temperature of exothermic reaction. (centigrade)*
H-bentonite	70-260	94.72	600-750	22	
Li- ,,	80-230	51.42	600-720	18	
Na- ,,	90-190	40.59	600-750	18	
K- ,,	70-180	32.00	600-720	20	*
Mg- ,,	80-270	97.28	600-740	22	
Ca- ,,	60-230	85.78	600-740	21	
Ba- ,,	70-220	55.04	600-760	18	

*As the peaks are not well defined the peak temperatures are not given.

beats of reaction for the desorption of interlayer water from the different complexes, the areas of the dehydroxylation peaks and also the peak temperatures of the exothermic reactions.

TABLE 5. RELATIVE HUMIDITY=25%, TEMPERATURE=23°C.

Complexes of bentonite from Hanover.	Desorption temperature in d.t.a. (centigrade)	Heats of desorption (ΔH) (cal/gm).	Dehydroxylation temperature in d. t. a. (centigrade)	Peak area of dehydroxylation (sq. mm.)	Peak temperature of exothermic reaction. (centigrade)
H-bentonite	43-233	107.52	613-733	18	933
Li- „	43-233	74.24	613-723	22	939
Na- „	53-213	66.56	623-753	22	948
K- „	53-203	58.88	613-753	26	953
Mg- „	53-253	120.32	653-773	20	949
Ca- „	43-253	96.00	613-753	20	953
Ba- „	43-223	73.75	623-763	26	961

TABLE 6. RELATIVE HUMIDITY=30%, TEMPERATURE=28°C.

Complexes of bentonite from Assam	Desorption temperature in d.t.a. (centigrade)	Heats of desorption (ΔH) (cal/gm)	Dehydroxylation temperature in d. t. a. (centigrade)	Peak area of dehydroxylation (sq. mm.)	Peak temperature of exothermic reaction. (centigrade)
H-bentonite	60-200	51.20	500-650	45	960
Li- „	55-220	28.16	500-630	44	968
Na- „	70-170	19.20	500-640	45	983
K- „	70-150	14.08	500-630	43	996
Mg- „	60-330	76.80	500-640	44	983
Ca- „	60-330	51.20	500-630	46	988
Ba- „	60-200	28.16	500-640	44	993

The determined values of the heats of reaction in Kcal/equivalent are plotted against the heats of hydration* of the monovalent and the divalent cations in figures 2-6. The relation obtained in the graphs is linear and the slopes of the straight lines are nearly the same in each group for

* The values are taken from *Electrochemical Data* by B. E. Conway Ph. D., D. I. C., *Elsevier Publishing Co.*, 1952.

TABLE 7

Complexes of bentonite from Rajasthan.	Desorption temperature in d.t.a. (centigrade)	Heats of desorption. (ΔH) (cal/gm.)	Dehydroxylation temperature in d. t. a. (centigrade)	Peak area of dehydroxylation (sq. mm.)	Peak temperature of exothermic reaction. (centigrade)
H-bentonite	38-218	81.92	428-578	16	928
Li- ,,	68-258	61.44	500-618	18	*
Na- ,,	58-218	51.20	518-628	16	933
K- ,,	68-208	44.80	508-628	16	*
Mg- ,,	38-298	76.80	478-588	16	918
Ca- ,,	48-228	67.84	508-628	18	925
Ba- ,,	58-228	43.52	500-618	17	960

*As the peaks are not well defined the peak temperatures are not given.

all the samples over the observed range of relative humidity. Thus, it may be said, that the mechanism of desorption of water from both divalent and monovalent cation saturated bentonites appears to be closely similar.

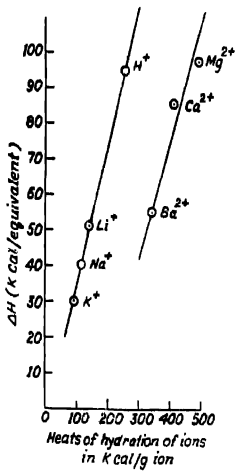

Figure 2. Variation of ΔH for salts of bentonite from England with heats of hydration of cations.

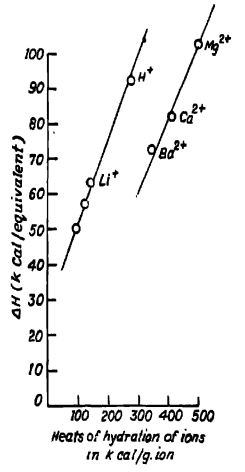

Figure 3. Variation of ΔH for salts of bentonite from Hanover with heats of hydration of cations.

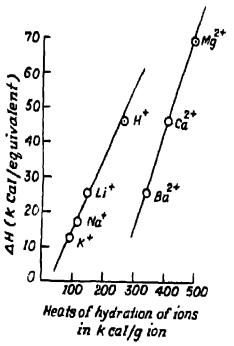

Figure 4. Variation of ΔH for salts of bentionite from Assam with heats of hydration of cations.

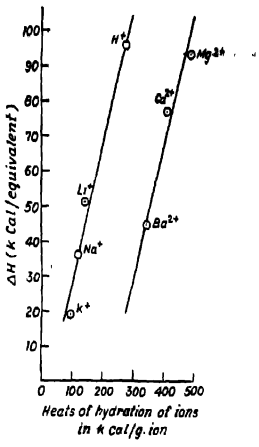

Figure 5. Variation of ΔH for salts of bentonite from Kashmir (pink variety) with heatsof hydration of cations.

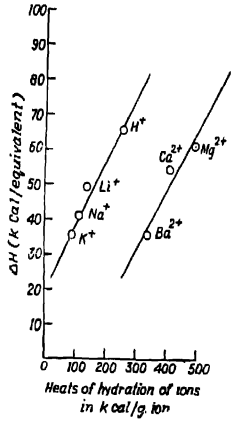

Figure 6. Variation of ΔH for salts of bentonite from Rajasthan with heats of hydration of cations.

The areas of the dehydroxylation peaks, shown in tables 3-7, are found to be nearly constant for a group of complexes derived from a particular bentonite, suggesting that the exchangeable cations have little or no influence on the dehydroxylation process. This is consistent with the idea that the OH-binding capacity is a characteristic physical constant of the material depending on the composition of the silicate layer and not on the exchangeable cations.

The peak temperatures of the exothermic reactions, given in tables 3-7, increase with the size of the cations having the same charge. The peak temperatures may also indicate the order of the energy associated with the rearrangement of the atoms as they shift to their new positions in the corresponding crystalline phases formed.

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